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Thermal variation of magnetic properties of europium sulphate octahydrate and some crystal field reduced matrix elements

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In course of work on the analysis of magnetic properties of paramagnetic ions in crystal lattices it is felt that simultaneous explanation of all the phenomena e g , crystal absorption spectra, magnetic properties, EPR etc , connected with the Stark manifolds of the ions by the same crystalline electric field (CEF) is possible only if the observed values are of a high degree of precision It is all the more so in case of Eu^{3+} ion since theoretical analysis in this case is more complicated compared to the other ions of the group because the J level separations are of the same order as that of the Stark levels In the present communication we report the observed values of the magnetic properties of $Eu_2(SO_4)_3$ $8H_2O$ which are obtained using refined techniques

The freshly grown single crystal of europium sulphate used in the measurements was checked carefully under a polarizing microscope and was found to have sharp extinctions. Improved technique (Neogy *et al* 1967) for the measurement of magnetic anisotropy was employed For absolute susceptibility a modified electromagnetic balance (Neogy & Lal 1962) was used wherein the balance coil was placed in the field of a local magnet since the balance was removed far from the vicinity of the electromagnet to avoid the effects of the field on the weights required to counterbalance the sample Current in the magnet was controlled with a stabilized power supply and a sensitive friction free current indicator. A modified liquid air bath cryostat (Bose *et al* 1963) was used to hold the temperature inside the crystal chamber steady at any desired value ($\sim\pm0\ 2$K) using an electronic temperature controller (Neogy & Neogy 1975) with which the temperature could be preset The smoothed curve values of the results appear in table 1. χ_3 is the principal susceptibility along crystallographic b-axis θ the angle between χ_2 and a-axis was found to be 74° which remained unchanged in the temperature range studied The mean square effective Bohr magneton numbers $p_{eff}^2 = 7{\cdot}9958\ \bar{\chi}T/2$ are also given We find that higher precision in the present measurements has led to a marked improvement over the earlier results (Neogy & Mookherji 1965c; the second column in table 1 in the paper should read $(\chi_1-\chi_2)+(\chi_3-\chi_2)$ and ΔK would change accordingly); there is also a lurking doubt that probably all was not well with the crystal used in the previous work.

Following earlier work (Neogy 1963, Neogy & Mookherji 1965a, b) if we take the paramagnetic cluster to have tetragonal symmetry in the first approximation, we find the ionic anisotropy $\Delta K = K_{11}-K_{\perp} = -((\chi_1-\chi_2)+(\chi_1-\chi_3))/2$ to be negative unlike other rare earth ions. The ΔK values are also given in table 1. It may be mentioned here that a rough theoretical estimate of ΔK also gives similar results; in course of this work the CEF reduced matrix elements (operator equivalent factors) for Eu^{3+} ion in the pure LS scheme for $J=1$ and $J=2$ states and also for the CEF intermixing (Elliot & Stevens 1953) of $|J=1\rangle$ with $|J=2\rangle$ were worked out by evaluating the matrix elements in $L\,S\,J\,J_z$, $L\,S\,L_z\,S_z$ and $l\,s\,l_z\,s_z$ schemes successively and then comparing them; the Clebsch Gordan coefficients involved in the expansions were calculated using standard relations. The sign of the reduced element in the intermixing case is dependent on the relative phases of $|J\rangle$ and $|J+1\rangle$ states and for this we have adopted the convention followed by Condon & Shortley (1957) with $J_{1z} = L_z$; the values of the reduced elements are given in table 2 in the notation of Stevens (1952) and Elliot & Stevens (1953).

Analysis of the observed data is in progress and would be reported in due course

Table 1 The smoothed curve values of principal anisotropies and χ_1 of $Eu_2(SO_4)_3 \cdot 8H_2O$ in cm^3 (g mol wt)$^{-1}$ 10^{-6} and $p_{eff}^2 = 7.9958\ T(\chi_1+\chi_2+\chi_3)/6$ (χ_1 values are corrected for diamagnetism)

Temp. (°K)	$\chi_1-\chi_2$	$\chi_1-\chi_3$	χ_1	p_{eff}^2	$-\Delta K$
300	780	925	9300	10 47	853
280	790	966	9400	9.87	878
260	820	1008	9575	9.32	914
240	900	1093	9825	8.79	996
220	1230	1257	10380	8.39	1244
200	1550	1484	11025	8 00	1517
180	1820	1728	11650	7.53	1774
160	2040	2004	12175	6.93	2022
140	2250	2319	12550	6.17	2284
120	2830	2680	13025	5 37	2755
100	3330	3015	13410	4.52	3173
90	3540	3140	13425	4.03	3340

Table 2

$\langle J=1\|\alpha\|J=1\rangle$	$\langle J=2\|\alpha\|J=2\rangle$	$\langle J=2\|\beta\|J=2\rangle$	$\langle J=2\|\alpha\|J=1\rangle$
$\frac{-1}{5}$	$\frac{-11}{3^2.5.7}$	$\frac{-2}{3^3.7}$	$\frac{1}{5.3^{\frac{1}{2}}}$

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